Synthesis and thermal treatment of cu-doped goethite: Oxidation of quinoline through heterogeneous fenton process

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A B S T R A C T

Samples of Cu-doped goethites were prepared and characterized by Mössbauer spectroscopy, XRD, TPR and BET surface area measurements. Mössbauer data showed the incorporation of Cu^{2+} in the goethite structure, and this cation-doping caused a significant decrease of the chemical reduction temperature in the TPR process. The catalytic behavior of these $Fe_{1-x}Cu_xOOH$ materials was investigated for the H_2O_2 decomposition to O_2 and the Fenton-like reaction to oxidize quinoline. It was observed that Cu^{2+} in this goethite and also the thermal treatment with H_2 produced a strong increase in the catalytic activity during the quinoline oxidation. The successive hydroxylation of quinoline during this oxidation strongly suggests that highly reactive hydroxyl radicals are generated during the reaction involving H_2O_2 on the Cu-goethite grain surface, also confirming that these materials are efficient heterogeneous Fenton catalysts.

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1. Introduction

Goethite (α-FeOOH) structurally consists of double bands of edge-sharing $FeO_3(OH)_3$ octahedra. The double bands are linked by corner-sharing in such a way as to form 2×1 octahedra "tunnels" crossed by hydrogen bridges [1]. The yellow-brown goethite occurs in almost all soils and other iron-containing surface formations. Its relative wide availability and suitable physical and chemical properties have allowed consideration of its use as a heterogeneous catalyst or starting material for catalysis of various industrial processes, including NH_3 synthesis, high temperature water–gas shift reaction to produce hydrogen, and desulphurization of natural gas [1]. To achieve the desirable catalytic activity the iron oxide should often be modified, dispersed on a supporting material or doped with some cations. Doping-cations are added to principally assist special redox processes, such as the Fenton reaction. The classical Fenton reaction ($Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^-OH + {}^{\bullet}OH$), involving hydrogen peroxide and Fe^{2+} in solution, is often used to degrade contaminants, such as industrial wastewater textile dyes [2,3]. In order to minimize the amount of the ferric hydroxide sludge forming in the homogeneous reaction, some iron oxides, such as magnetite (ideal formula, Fe_3O_4), hematite (α-Fe_2O_3), goethite (α-FeOOH) or ferrihydrite ($Fe_5HO_8 \cdot 4H_2O$), are used instead, as heterogeneous

catalysts [4]. For this reason, active heterogeneous redox processes are increasingly replacing the homogeneous systems in catalysis research [5–9] and in some technological applications, particularly for environmental remediation. Modifications of the iron oxide structure by doping with isomorphic cations or by thermal treatment have been studied by many authors, in an attempt to improve the catalytic performance of those materials. However, to date, the chemical role of Fe^{3+}, Fe^{2+} and other ions and their ability to promote the production of the $^{\bullet}OH$ radical are not sufficiently clear [10].

It is well known that nitrogen-containing impurities are significant sources of atmospheric pollution, as well as being potential agents of acid rain. In this context there is a search for new technologies that can better satisfy environmental requirements.

In this work, quinoline was used as a model compound present in the diesel fuel, aiming to shed some light on the chemical mechanisms involved in the oxidative reaction. The effect of thermal treatment under a H_2 stream on the surface of goethite and also of copper-doped goethites ($Fe_{1-x}Cu_xOOH$, $x = 0.05$) on the Fenton oxidation of quinoline was evaluated.

2. Experimental

2.1. Catalyst preparation and characterization

All chemicals were high purity grade and were used as purchased. A goethite sample was prepared by co-precipitation,

starting from $Fe(NO_3)_3 \cdot 6H_2O$ (1.7 mol L^{-1}) and NaOH (1 mol L^{-1}) followed by thermal treatment at 60 °C (72 h). The Cu substituted goethite (GtCu) was prepared from $Fe(NO_3)_3 \cdot 6H_2O$ (1.7 mol L^{-1}) and $CuSO_4$ (Merck) solution (0.35 mol L^{-1}) by precipitation with sodium hydroxide (1.0 mol L^{-1}). The precipitates were washed with water until pH 7, dried at 80 °C for 12 h.

The synthetic samples were then ground and sieved to 100 mesh (Tyler series), dried for 1 h at 120 °C. After that, part of the GtCu sample was heated up to 350 °C for 3 h (reduced GtCu) at 20 °C min^{-1} under a H_2, at a flow rate of 50 mL min^{-1}, in a tubular furnace. All chemical reactants used were obtained from Aldrich or Merck and used as received. To perform oxidation tests, 0.1 mL of H_2O_2 30% (v/v) and 30 mg of these goethite samples were added to the aqueous solutions (prepared with Millipore MilliQ graded water) of quinoline (3.5 mL at 0.05 g L^{-1}) under stirring and nearly constant temperature, at 25 ± 1 °C.

The surface area was determined with the BET method using N_2 adsorption/desorption in an Autosorb 1 Quantachrome instrument. Mössbauer spectroscopy experiments were carried out at room temperature in a spectrometer model MA250 with a $^{57}Co/Rh$ source, using an αFe foil as reference. The powder XRD data were obtained in a Rigaku model Geigerflex using Co $K\alpha$ radiation scanning from 10° to 80° 2θ at a scan rate of 4° min^{-1}. TPR experiments were performed in a CHEMBET 3000 equipment with 20 mg_{sample} under 80 mL min^{-1} H_2 (5%)/N_2 with heating rate of 10 °C min^{-1}. Pure, GtCu and reduced GtCu samples were analysed by FTIR using an Excalibur FTS3000 from Bio Rad.

2.2. Catalytic tests

The catalytic properties of the material were tested via oxidation of quinoline. The oxidation tests were carried out using 9.9 mL of a quinoline solution (10 mg L^{-1}) in water. 10 mg of the catalyst were used and also H_2O_2 (VETEC, 30%) as oxidant. The reaction progress of quinoline oxidation was monitored with electrospray ESI-MS (Agilent-1100), allowing to identify intermediates formed during this reaction. ESI-MS/MS experiments in the positive ion mode were performed.

Total organic carbon (TOC) measurements were carried out in TOC 500A Shimadzu.

2.2.1. ESI-MS study

The quinoline (10 mL from a 50 mg L^{-1} stock solution) decomposition was monitored using electrospray ionization mass spectrometry (ESI-MS), in an attempt to identify the intermediately formed chemical species. The reaction samples were analysed by introducing aliquots into the ESI source with a syringe pump at a flow rate of 5 μL min^{-1}. The spectral data so obtained were averaged from 50 scans of 0.2 s each. Typical ESI-MS conditions were as follows: heated capillary temperature, 150 °C; dry gas (N_2) at a flow rate of 5 L min^{-1}; spray voltage, 4 kV; capillary voltage, 25 V; tube lens offset voltage, 25 V. For ESI-MS/MS, the parent ion of interest was first isolated by applying an appropriate waveform across the end cap electrodes of the ion trap to resonantly eject all trapped ions, except those ions with m/z ratio of interest. The isolated ions were then subjected to a supplementary AC signal, to resonantly excite them causing collision-induced dissociation (CID) using helium as a reagent gas.

3. Results and discussion

3.1. Characterization of the goethites

Fig. 1 shows the infrared spectra of prepared goethite and CuGt samples. A typical signal for this goethite is an intense band due to the bulk O–H stretch, which is observed at 3114 cm^{-1}.
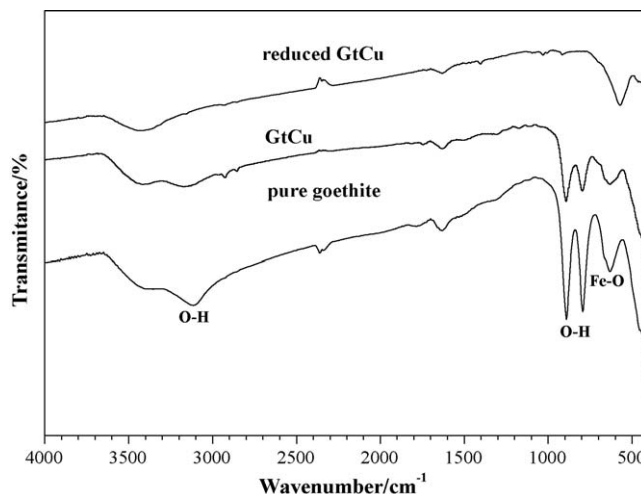

Fig. 1. Infrared spectra of the materials after treatments.

Moreover, O–H bending signals at 799 and 902 cm^{-1}, which vibrate in and out of the plane, respectively, are important diagnostic bands, characteristic of goethite. It can be observed that these two bands disappear after thermal treatment. These results and the Fe–O vibration band at $ca.$ 573 cm^{-1} suggest that some magnetite may have been formed.

Corresponding XRD patterns (Fig. 2) suggest the occurrence of poorly crystalline goethite-like phase in the pure and GtCu samples with broad reflections. Values of a-lattice parameters were determined as being 0.215, 0.215 and 0.136 nm for pure, GtCu and reduced GtCu, respectively. XRD data also indicate that the thermal treatment under H_2 flow causes the reduction of all goethite to magnetite, producing a characteristic cubic structure pattern. Moreover, the presence can also be observed of a small amount of a metallic iron phase.

Mössbauer spectra for these materials are presented in Fig. 3a. In the case of pure goethite, the sample is probably formed by small particle-sized iron hydroxide grains evidenced by a strong (super) paramagnetic central doublet along with a narrow-line-sextet, corresponding to a hyperfine field (B_{hf}) of 36.0 T. The super-paramagnetic behavior of goethite has been attributed to a relatively high concentration of vacancy defects [11]. The spectrum for the GtCu sample also presents an intense effect of a putative super-paramagnetism; the hyperfine field (B_{hf} = 31.5 T) for this sextet is
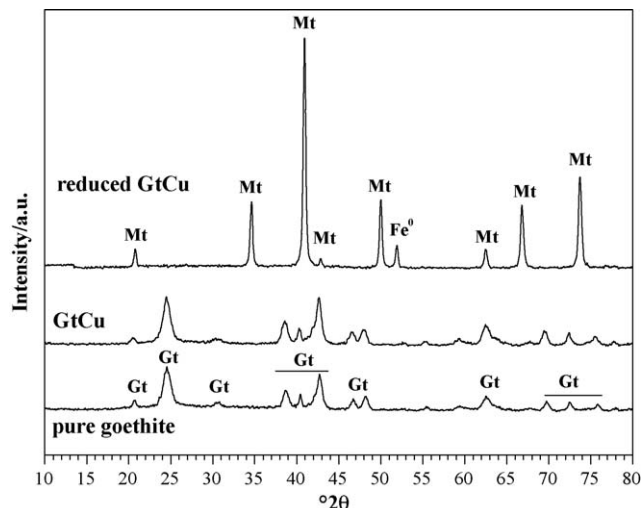

Fig. 2. XRD analyses of pure and modified goethites.

Table 1
Mössbauer parameters obtained from the fit of the room temperature (~298 K) spectra of pure, doped and doped after reduction goethites.[a]

Sample	^{57}Fe site	δ (mm s^{-1})	ε (mm s^{-1})	B_{hf} (T)	RA (%)
Pure goethite	Gt	0.34(3)	−0.271(5)	36.0[b]	100
GtCu	Gt	0.38(3)	−0.224 (9)	31.5[b]	100
Reduced GtCu	Mt-A	0.30(2)	−0.029(4)	48.8(2)	43
	Mt-B	0.54(2)	0.031(6)	46.0[b]	40
	Fe^0	0.0003[c]	0[c]	33.0[c]	6
	Mh	0.34[c]	0.028[c]	50.4(5)	11

[a] Gt = goethite; Mt = magnetite; Mh = maghemite; A and B—representations for tetrahedral and octahedral coordination sites in the spinel structure, respectively; δ = isomer shift with respect to αFe, ε = quadrupole shift, B_{hf} = magnetic hyperfine field, eRA = relative sub-spectral area.
[b] Maximum fields of the distribution
[c] Fixed parameters

much lower in this case than it is for the goethite sample. This result is in line with previously reported data for doped goethite [12]. The room temperature Mössbauer spectrum for the H$_2$-reduced GtCu clearly shows tetrahedral (A) and octahedral (B) sites of magnetite, with B_{hf} = 48.8 and 46 T, respectively. A magnetic spectral-set corresponding to B_{hf} = 50.43 T, δ = 0.34 mm s^{-1} with a relative spectral area of 11% also suggest the occurrence of some maghemite γFe$_2$O$_3$ (Table 1).
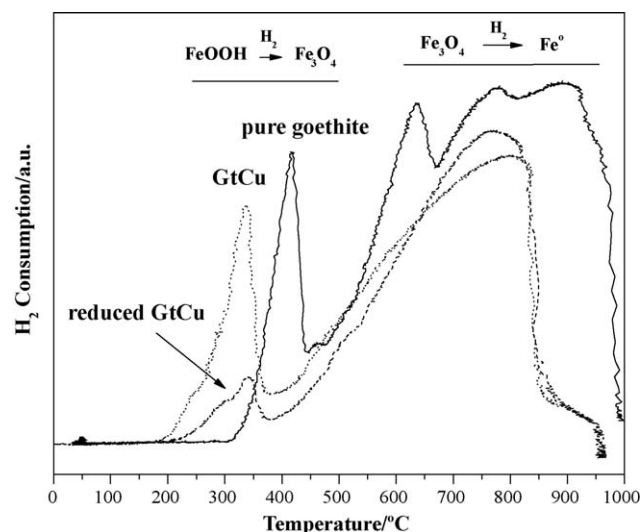
Fig. 4. Temperature-programmed reduction profile of the materials.

Focusing more attention now on the magnetic spectral sextets, the field distributions (Fig. 3b) lead to at least three main hyperfine fields for each of the two non-reduced samples. However, all values
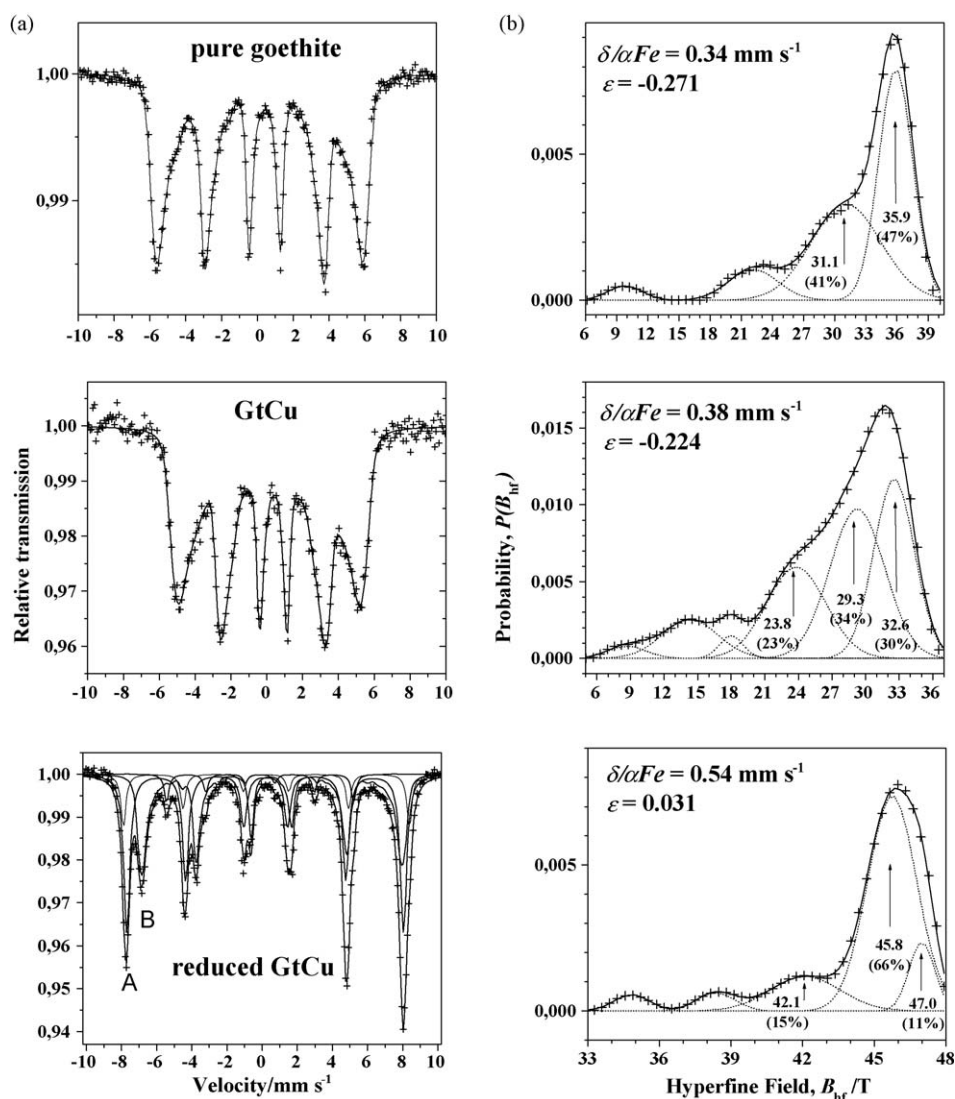
Fig. 3. (a) Mössbauer spectra and (b) corresponding hyperfine field distribution for goethite, Cu-goethite and H$_2$-reduced Cu-goethite.
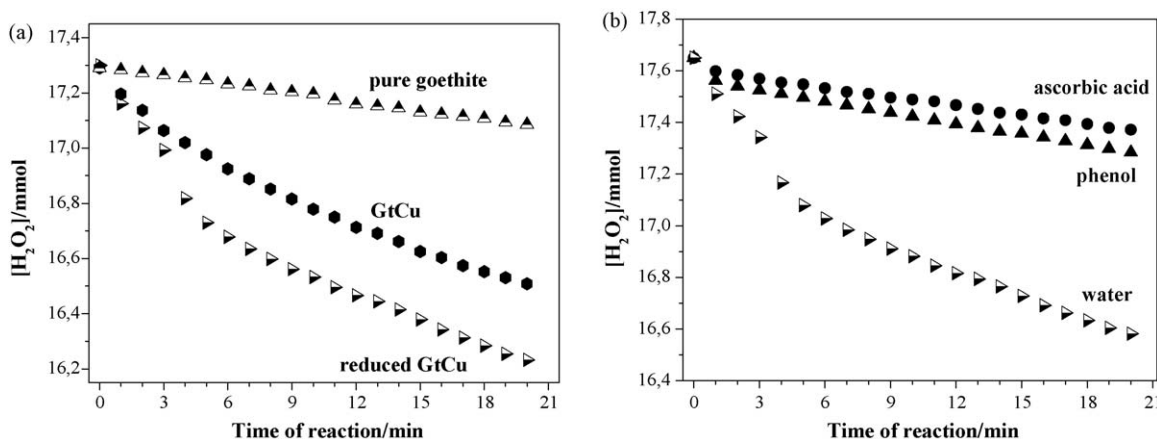
Fig. 5. Decomposition of H_2O_2 in presence of modified goethites in water (a) and in presence of some organic substrates (b).

are all approximately similar for both cases. The corresponding $Fe^{3+/2+}$-distribution for the H_2-reduced CuGt, with a relatively sharper probability profile, is also shown.

The temperature-programmed reduction (TPR) in Fig. 4 profile of the pure goethite presented a peak centred at 418 °C with a broad peak from 550 to 800 °C. The first peak is typical for the formation of magnetite, typical iron oxide with structural Fe^{2+}. The GtCu presented a strong decrease in the temperature (336 °C) of magnetite formation. The TPR profile of the reduced GtCu showed a small peak due to Fe^{3+}, suggesting the formation of an iron reduced phase after the thermal treatment under H_2 atmosphere.

3.2. Catalytic tests

3.2.1. H_2O_2 decomposition

The catalytic activity of the goethite series was studied using two reactions: (i) the H_2O_2 decomposition (Eq. (1)):

$$H_2O_2 \rightarrow H_2O + O_2 \tag{1}$$

and (ii) the oxidation of quinoline with H_2O_2 in aqueous medium. The H_2O_2 decompositions in the presence of different goethites are presented in Fig. 5. It is observed that the GtCu materials and reduced GtCu strongly favored the H_2O_2 decomposition (Fig. 5a). The decomposition kinetics is a complex reaction, the linear behavior of the decomposition plots, in the first minutes, suggests that the process can be approximate to pseudo-zero order kinetics. The literature shows that the incorporation of metal by isomorphic substitution and/or the conversion of Fe^{3+} sites to Fe^{2+} enhances
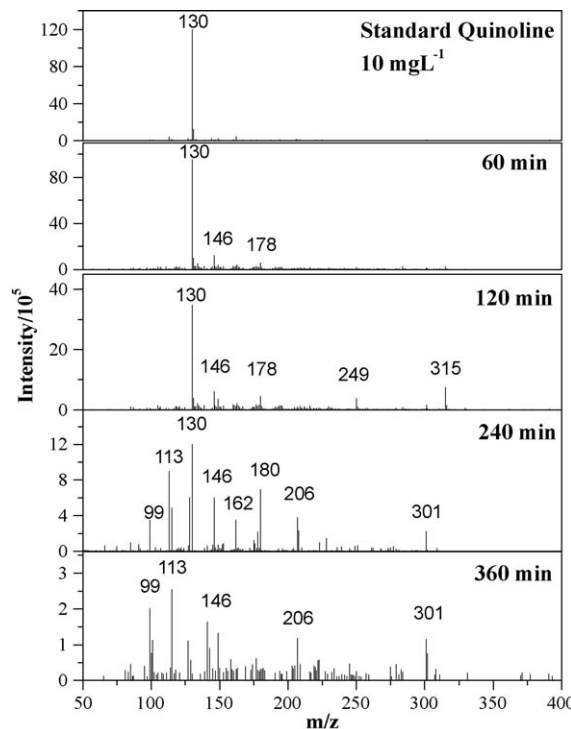

Fig. 6. Electrospray ionization mass spectrometry (ESI-MS) in the positive ion mode for monitoring the oxidation by the reduced GtCu//H_2O_2 system of quinoline in water.
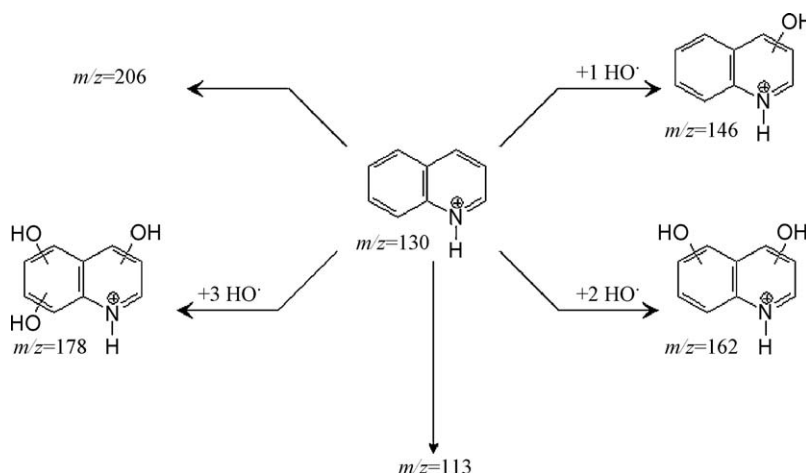

Fig. 7. Scheme with proposed intermediates for the oxidation of quinoline ($m/z = 130$) by the catalyst.
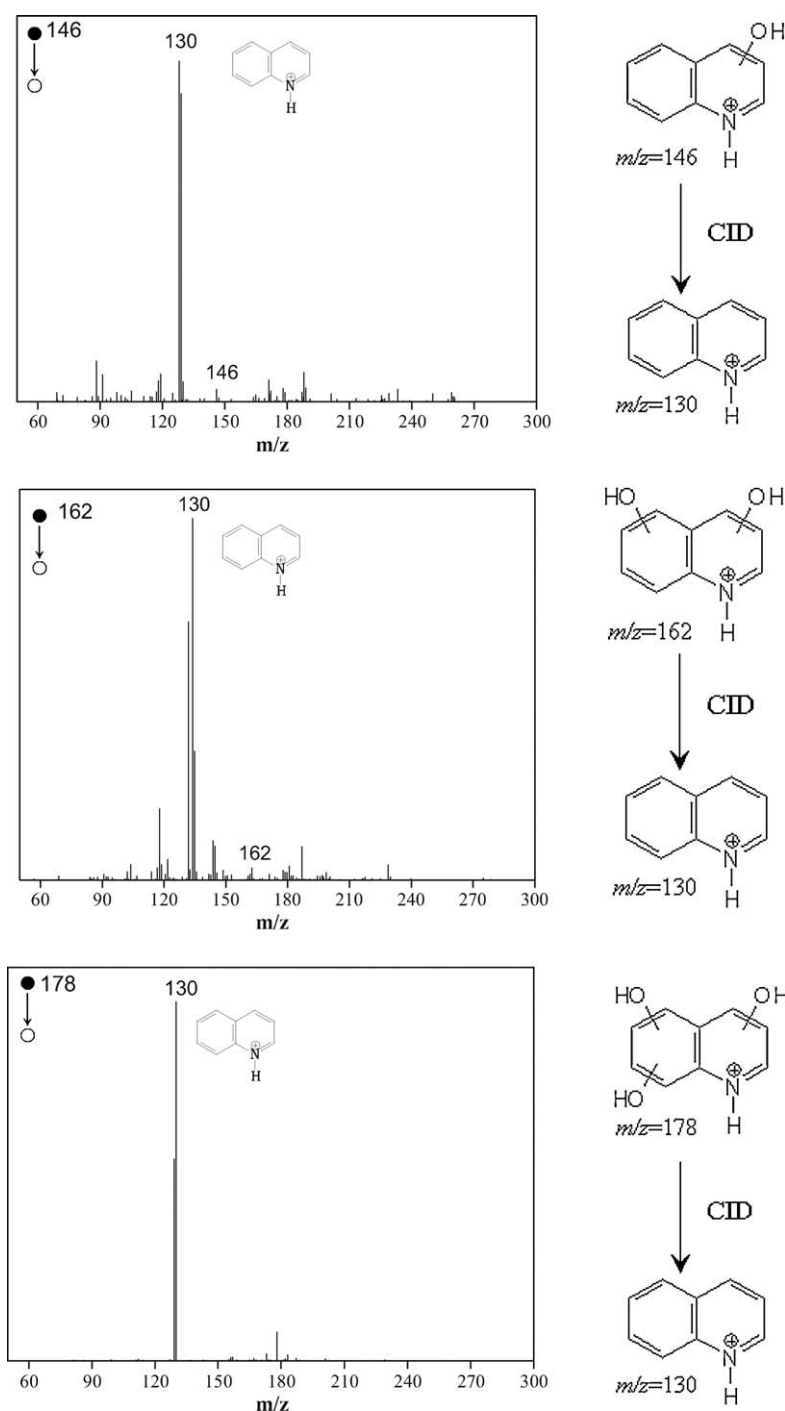
Fig. 8. Electrospray ionization mass spectrometry (ESI-MS/MS) spectrum of the m/z intercepted during the oxidation of quinoline in water by the reduced GtCu/H_2O_2 system. *CID = collision-induced dissociation.

H_2O_2 decomposition rate probably due to textural and/or surface modifications [13]. Accordingly, the present work shows higher hydrogen peroxide decomposition rate over surface containing copper and iron (doped and reduced sample) when compared to the surface containing only Fe^{3+} species.

Fig. 5b shows the H_2O_2 decomposition utilizing the most active catalysts, reduced GtCu, in the presence of two organic compounds (ascorbic acid and phenol). It also can be observed that the H_2O_2 decomposition is strongly inhibited by the presence of another organic compound (ascorbic acid or phenol). The reaction inhibition might be due to a competitive process involving the organic substrate and the active surface that could

be related to the adsorption of the organic compounds on the active sites of the composite and their reactions with intermediate species in the H_2O_2 decomposition reaction. Moreover, a possible mechanism can be based on the activation of H_2O_2 via a Haber Weiss mechanism to form a radical HO• [13]. This radical can react by two competitive pathways: the oxidation of an organic molecule or the O_2 formation via the radical HOO•. Thus, the presence of ascorbic acid and phenol (radical scavengers) can be quenching the radical intermediates decreasing the rate of O_2 formation.

To investigate the possibility of homogeneous reactions produced by Fe and Cu species leached from the GtCu and reduced
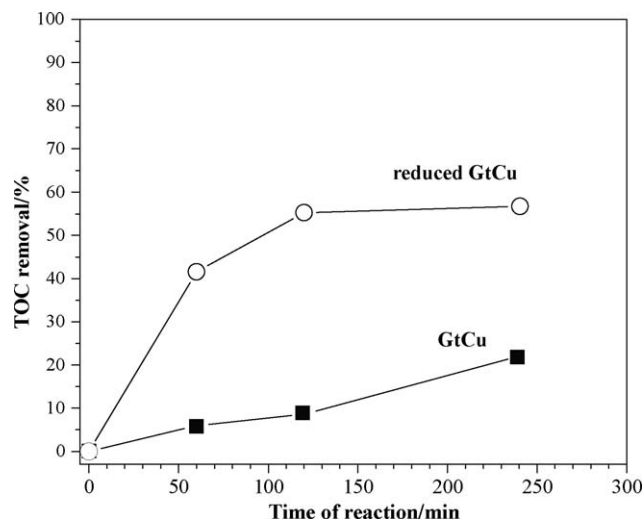
Fig. 9. Total organic carbon analyses for the GtCu and reduced GtCu samples.

GtCu to the aqueous medium, atomic absorption analyses were carried out in the aqueous phases after all the reactions. The obtained concentrations of Fe and Cu were all below the detection limit of the atomic absorption equipment.

3.2.2. Quinoline oxidation in the presence of H_2O_2

The quinoline oxidation by the most active catalyst for H_2O_2 decomposition, i.e. the reduced GtCu sample, was studied. The ESI-MS spectrum obtained for the quinoline solution only shows a strong signal at $m/z = 130$, which is related to the protonated quinoline (Fig. 6). After 240 min of reaction with the reduced GtCu and hydrogen peroxide, some new and strong m/z signals appear, specifically at 146, 162, 180 and 194, which may indicate hydroxylation steps. At this reaction time, the m/z signals appearing at $m/z = 85$, 99 and 113 are assumed to be related to quinoline oxidation intermediates, from fragmentations of the molecular structural ring.

The results obtained in this work suggest that the Cu in the goethite structure and the thermal treatment under H_2 flow strongly favors the H_2O_2 decomposition with radical as intermediates and consequently the oxidation of quinoline with successive hydroxylations. A work in the literature suggested that Cu^+ could participate in a Haber Weiss mechanism to generate $HO^\bullet$ free radicals [14]. The thermal treatment can be to reduce the Fe^{3+} from goethite as well as the Cu^{2+}, improving the radical formation as suggested by the following equations:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^\bullet + OH^- \tag{2}$$

$$Cu^{1+} + H_2O_2 \rightarrow Cu^{2+} + HO^\bullet + OH^- \tag{3}$$

These results also indicate that the Fenton oxidation mechanism ($^\bullet$OH attack) is taking place to a significant extent. The schematic structures for the hydroxylated intermediates from quinoline oxidation are proposed in Fig. 7.

To test the structural assignments for intermediates showed in Fig. 7, ESI-MS/MS spectra were acquired. Fig. 8 displays the ESI-MS/

MS spectra for the structure after many hydroxylations ($m/z = 146$, $m/z = 162$, etc.). Those mass values support the structural assignments of Fig. 7 as an *OH attack suggesting that a Fenton reaction takes place in heterogeneous phase [15].

Fig. 9 shows the TOC removal for the most active samples, i.e. GtCu and reduced GtCu, at different reaction times. It can be observed that the treatment with hydrogen flow produced a higher TOC removal (approximately 57% removal) than the material only after impregnation with copper, suggesting that the presence of reduced phases might play a role in the removal process. It is interesting to comment that the TOC removal obtained with these materials was much better than many reaction processes studied from some authors [4,15,16] attesting that the goethite with copper, after thermal treatment with H_2 flow, is a good catalyst in the oxidation of a important organic pollutant such as quinoline.

4. Conclusions

The presence of Cu associated with a thermal treatment under H_2 flow has a significant effect on the catalytic activity of the oxide. In this study, the oxidation of organic compounds with H_2O_2 has been shown to probably take place via radicals, as suggested by ESI-MS data. An oxidation mechanism was indicated to occur by attack of the free radical *OH on the molecule, giving rise to hydroxylation products as principal by-products, although compounds resulting from ring cleavage are also detected. The presence of copper increases the activity of the oxide for the H_2O_2 decomposition, and the reduced species such as Cu^+ and Fe^{2+} surface species seem to act directly in the catalytic properties of the catalyst.

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